



(51) International Patent Classification ⁶ : C11D 3/00		A2	(11) International Publication Number: WO 96/06153
			(43) International Publication Date: 29 February 1996 (29.02.96)
(21) International Application Number: PCT/EP95/03211			(81) Designated States: AM, AU, BB, BG, BR, BY, CA, CN, CZ, EE, FI, GE, HU, IS, JP, KG, KP, KR, KZ, LK, LR, LT, LV, MD, MG, MK, MN, MX, NO, NZ, PL, RO, RU, SG, SI, SK, TJ, TM, TT, UA, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, MW, SD, SZ, UG).
(22) International Filing Date: 14 August 1995 (14.08.95)			
(30) Priority Data: 2611/94-8 25 August 1994 (25.08.94) CH			
(71) Applicant (for all designated States except US): CIBA-GEIGY AG [CH/CH]; Klybeckstrasse 141, CH-4002 Basle (CH).			
(72) Inventor; and (75) Inventor/Applicant (for US only): MOLDOVANYI, Laszlo [CH/CH]; Oberer Batterieweg 15, CH-4059 Basle (CH).			
(74) Common Representative: CIBA-GEIGY AG; Patentabteilung, Klybeckstrasse 141, CH-4002 Basle (CH).			Published <i>Without international search report and to be republished upon receipt of that report.</i>
(54) Title: SURFACE-ACTIVE FORMULATIONS			
(57) Abstract			
<p>The invention relates to surface-active soap formulations, comprising: (a) 0.01 to 5 % by weight of a microbicidal active substance selected from the group consisting of (a₁) phenol derivatives (a₂) diphenyl compounds (a₃) benzyl alcohols (a₄) chlorohexidine (a₅) C₁₂-C₁₄alkylbetaines and C₈-C₁₈fatty acid amidoalkylbetaines (a₆) amphoteric surfactants and (a₇) trihalocarbanilides; (b) 0.1 to 25 % by weight of one or more than one hydrotropic agent; (c) 0 to 10 % by weight of one or more than one synthetic surface-active substance or of a soap or of combinations of the cited substances; (d) 0 to 8 % by weight of a salt of a saturated and/or unsaturated C₈-C₂₂fatty acid; (e) 0 to 50 % by weight of a dihydric alcohol; (f) 0 to 70 % by weight of a monohydric alcohol or of a mixture of several monohydric alcohols; and (g) mains water or deionised water to make up 100 %, with the proviso that the formulations contain at least one of components (c) and (d). The formulations are used for the disinfection and cleansing of the human skin and hands and of hard objects.</p>			

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

Surface-active formulations

It is commonly knowledge that the antimicrobial/microbicidal properties of active substances in aqueous solutions of soaps or surfactants are strongly influenced by micell systems and may even be almost totally blocked.

Surprisingly, it has now been found that certain hydrotropic suppress the microbicidal inhibiting activity of the micells of soap and surfactant systems (so-called "deblocked surfactant systems"). Accordingly, the antimicrobial/microbicidal activity of different active ingredients can be significantly enhanced in many surfactant systems.

The novel surface-active surfactant formulations comprise

- (a) 0.01 to 5% by weight of a microbicidal active substance selected from the group consisting of
 - (a₁) phenol derivatives,
 - (a₂) diphenyl compounds,
 - (a₃) benzyl alcohols,
 - (a₄) chlorohexidine,
 - (a₅) C₁₂-C₁₄alkylbetaines and C₈-C₁₈fatty acid amidoalkylbetaines,
 - (a₆) amphoteric surfactants,
 - (a₇) trihalocarbanilides, and
 - (a₈) quaternary ammonium salts;
 - (b) 0.1 to 25% by weight of one or more than one hydrotropic agent;
 - (c) 0 to 10% by weight of one or more than one synthetic surface-active substance or of a soap or of combinations of the cited substances;
 - (d) 0 to 8% by weight of a salt of a saturated and/or unsaturated C₈-C₂₂fatty acid;
 - (e) 0 to 50% by weight of a dihydric alcohol;
 - (f) 0 to 70% by weight of a monohydric alcohol or of a mixture of several monohydric alcohols; and
 - (g) mains water or deionised water to make up 100%,
- with the proviso that the formulations contain at least one of components (c) and (d).

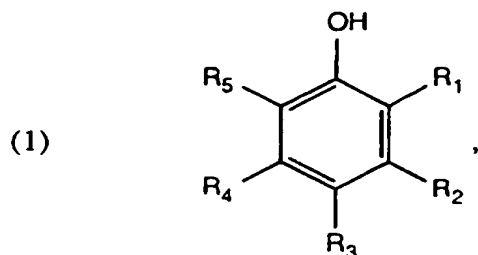
Soap formulations will be understood as meaning aqueous soap solutions which may be obtained as soap or so-called syndet solutions (= synthetic detergents).

The antimicrobial activity of the deblocked surfactant systems reaches upon gram-positive

- 2 -

and gram-negative bacteria as well as yeasts, dermatophytes and the like.

The compounds of component (a₁) preferably correspond to the general formula



wherein

R₁ is hydrogen, hydroxy, C₁-C₄alkyl, chloro, nitro, phenyl oder benzyl,

R₂ is hydrogen, hydroxy, C₁-C₆alkyl or halogen,

R₃ is hydrogen, C₁-C₆alkyl, hydroxy, chloro, nitro or a sulfo group in the form of the alkali metal salts or ammonium salts thereof,

R₄ is hydrogen or methyl,

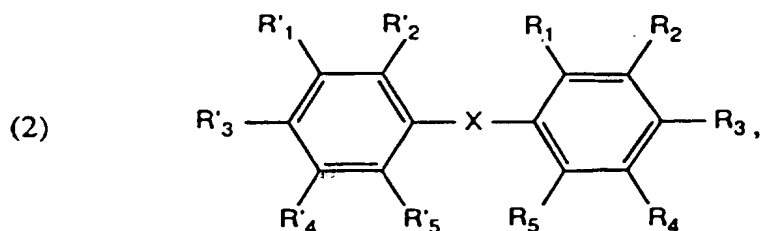
R₅ is hydrogen or nitro.

Halogen is bromo or, preferably, chloro.

Such compounds are typically chlorophenols (o-, m-, p-chlorophenols),

2,4-dichlorophenol, p-nitrophenol, picric acid, xylenol, p-chloro-m-xylenol, cresols (o-, m-, p-cresols), p-chloro-m-cresol, pyrocatechin, resorcinol, orcinol, 4-n-hexylresorcinol, pyrogallol, phloroglucine, carvacrol, thymol, p-chlorothymol, o-phenylphenol, o-benzylphenol, p-chloro-o-benzylphenol and 4-phenolsulfonic acid.

The compounds of component (a₂) preferably correspond to the general formula



wherein

X is sulfur or the methylene group,

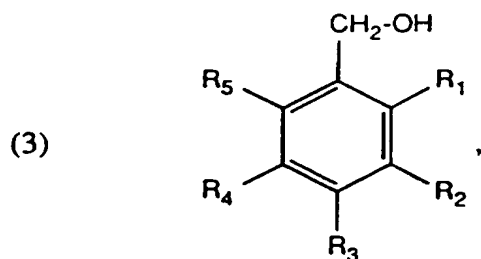
- 3 -

R_1 and R'_1 are hydroxy, and

R_2 , R'_2 , R_3 , R'_3 , R_4 , R'_4 , R_5 and R'_5 are each independently of one another hydrogen or halogen.

Typical examples of compounds of formula (2) are hexachlorophene, tetrachlorophene, dichlorophene, 2,3-dihydroxy-5,5'-dichlorodiphenylsulfide, 2,2'-dihydroxy-3,3',5,5'-tetrachlorodiphenylsulfide, 2,2'-dihydroxy-3,3',5,5',6,6'-hexachlorodiphenylsulfide and 3,3'-dibromo-5,5'-dichloro-2,2'-dihydroxydiphenylamine.

The compounds of component (a_3) preferably correspond to the general formula



wherein

R_1 , R_2 , R_3 , R_4 and R_5 are each independently of one another hydrogen or chloro.

Illustrative examples of compounds of formula (3) are benzyl alcohol, 2,4-, 3,5- or 2,6-dichlorobenzyl alcohol and trichlorobenzyl alcohol.

Component (a_4) is chlorohexidine and salts thereof together with organic and inorganic acids, which type of compound may preferably be incorporated into syndet systems.

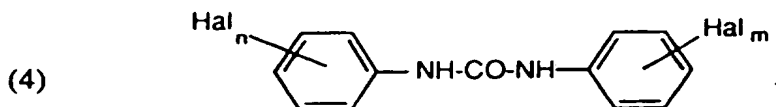
Component (a_5) is typically C_8 - C_{18} cocamidopropylbetaine.

Amphoteric surfactants corresponding to component (a_6) are suitably

C_{12} alkylaminocarboxylic and C_1 - C_3 alkanecarboxylic acids such as alkylaminoacetates or alkylaminopropionates.

The compounds of component (a_7) preferably correspond to the general formula

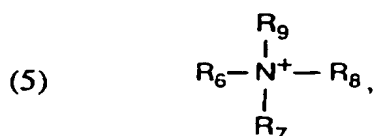
- 4 -



wherein

Hal is chloro or bromo,
 n and m are 1 or 2, and
 n + m are 3.

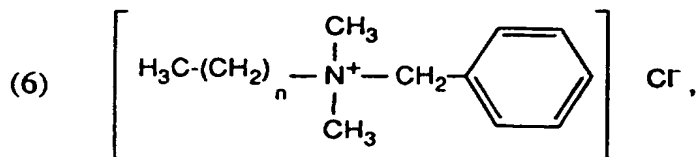
The quaternary ammonium salts of component (a_g) preferably correspond to formula



wherein

R₆, R₇, R₈ and R₉ are each independently of one another C₁-C₁₈alkyl, C₁-C₁₈alkoxy or phenyl-lower alkyl, and
 Hal is chloro or bromo.

Among these salts, the compound of formula



wherein

n is an integer from 7 to 17, is very particularly preferred.

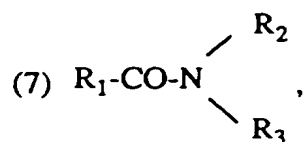
The following compounds are suitable for use as component (b):

- (b₁): sulfonates, preferably the salts thereof of terpenoids, or mono- or binuclear aromatic compounds, typically sulfonates of camphor, toluene, xylene, cumene or naphthene;
- (b₂): saturated or unsaturated C₃-C₁₂di- or polycarboxylic acids, typically malonic, succinic, glutaric, adipic, pimelic, suberic, azelaic and sebacic acid, undecanedicarboxylic acid and dodecanedicarboxylic acid, fumaric, maleic, tartaric

- 5 -

and malic acid as well as citric and aconitic acid;

- (b₃):
- aliphatic saturated or unsaturated C₁-C₁₁ monocarboxylic acids, typically acetic, propionic, hexanoic, capric or undecylenoic acid;
 - saturated or unsaturated C₃-C₁₂ di- or polycarboxylic acids, typically malonic, succinic, glutaric, adipic, pimelic, suberic, azelaic and sebacic acid, undecanecarboxylic and dodecanedicarboxylic acid, fumaric, maleic, tartaric and malic acid as well as citric and aconitic acid;
 - aminocarboxylic acids, typically ethylenediaminetetracetic acid, hydroxyethyl-ethylenediaminetetracetic acid and nitrilotriacetic acid;
 - cycloaliphatic carboxylic acids such as camphoric acid;
 - aromatic carboxylic acids, typically benzyl, phenylacetic, phenoxyacetic and cinnamic acid, 2-, 3- and 4-hydroxybenzoic acid, anilinic acid as well as o-, m- and p-chlorophenylacetic acid and o-, m- and p-chlorophenoxyacetic acid;
 - alkali metal salts and amine salts of inorganic acids, typically the sodium or potassium salts and amine(R₁R₂R₃) salts of hydrochloric, sulfuric, phosphoric, C₁-C₁₀alkylphosphoric acid and boric acid, in which amine salts R₁, R₂ and R₃ have the meaning indicated above;
 - isethionic acid;
 - tannic acid;
 - acid amides of formula



wherein

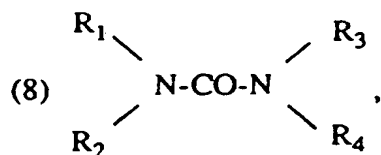
R₁ is hydrogen or C₁-C₁₂alkyl, and

R₂ and R₃ are each independently of the other hydrogen, C₁-C₁₂alkyl,

C₂-C₁₂alkenyl, C₁-C₁₂hydroxyalkenyl, C₂-C₁₂hydroxyalkyl, or a polyglycol ether chain containing 1 to 30 -CH₂-CH₂-O- or -CHY₁-CHY₂-O- groups, wherein

Y₁ or Y₂ is a hydrogen radical and the other is methyl, e.g. N-methylacetamide;

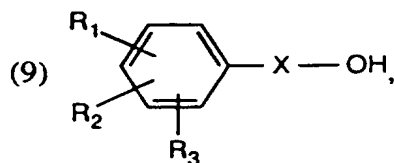
- urea derivatives of formula



- 6 -

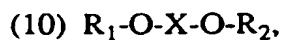
wherein

R_1 , R_2 , R_3 and R_4 are each independently of one another hydrogen, C_1 - C_8 alkyl, C_2 - C_8 alkenyl, C_1 - C_8 hydroxyalkyl or C_2 - C_8 hydroxyalkenyl;
 - monohydric C_4 - C_{18} aliphatic and monocyclic alcohols, typically C_2 - C_{18} alkanols, C_2 - C_{18} alkenols and terpene alcohols e.g. ethanol, propanol, isopropanol, hexanol, cis-3-hexen-1-ol, trans-2-hexen-1-ol, 1-octen-3-ol, heptanol, octanol, trans-2-cis-6-nonadien-1-ol, decanol, linalol, geraniol, dihydroterpineol, myrcenol, nopol and terpineol;
 - aromatic alcohols of formula



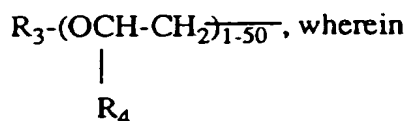
wherein

X is $-(CH_2)_{1-6}$, $-CH=CH-CH_2-$, or $-O-(CH_2)_{2-6}$, and
 R_1 , R_2 and R_3 are each independently of one another hydrogen, hydroxy, halogen or C_1 - C_6 alkoxy, typically benzyl alcohol, 2,4-dichlorobenzyl alcohol, phenoxyethanol, 1-phenoxy-2-propanol (phenoxyisopropanol) and cinnamyl alcohol;
 - polyhydric alcohols and polyhydric alkoxyated, preferably ethoxylated and/or propoxylated alcohols as well as the ethers and esters thereof of the general formula



wherein

R_1 and R_2 are each independently of the other hydrogen, C_1 - C_{12} alkyl, C_2 - C_{12} alkenyl, C_1 - C_8 alkanoyl, C_3 - C_{18} alkenoyl,

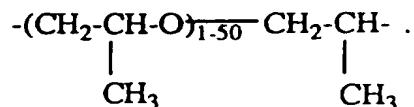


R_3 is hydrogen, C_1 - C_{12} alkyl or C_2 - C_{12} alkenyl, and

R_4 is hydrogen or $-CH_3$, and

X is C_2 - C_{10} alkylene or C_2 - C_{10} alkenylene, $-(CH_2CH_2O)_{1-50}CH_2-CH_2-$ or

- 7 -



All organic acids mentioned under (b) may also be obtained in the form of their water-soluble salts, such as the alkali metal salts, preferably the sodium or potassium salts or the amine(NR₁R₂R₃) salts, wherein

R₁, R₂ and R₃ are each independently of one another hydrogen,

C₁-C₈alkyl, C₂-C₈alkenyl, C₁-C₈hydroxyalkyl, C₅-C₈cycloalkyl or polyalkenylenoxy-C₁-C₁₈alkyl, or

R₁, R₂ and R₃, together with the linking nitrogen atom, are unsubstituted or C₁-C₄alkyl-substituted morpholino.

Component (b) can consist of only one compound of subclass (b₁) or also of mixtures of one or more than one compound of subclass (b₁), also together with components of further subclasses.

A special antimicrobial activity is achieved with a combination of one or more than one compound of subclass (b₁) and one or more than one compound of subclass b₂).

Particularly preferred in this connection is a combination of cumene sulfonate and citric acid monohydrate.

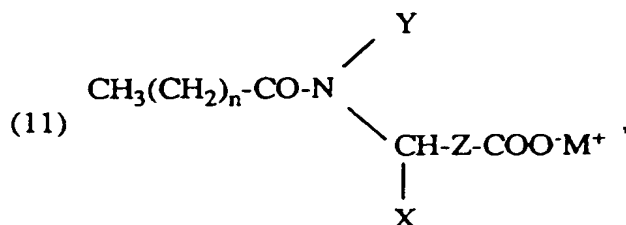
Suitable components (c) are anionic, nonionic or zwitterionic and amphoteric synthetic, surface-active substances.

Suitable anionic surface-active substances are:

- sulfates, typically fatty alcohol sulfates, which contain 8 to 18 carbon atoms in the alkyl chain, e.g. sulfated lauryl alcohol;
- C₈-C₂₂fatty alcohol ether sulfates, typically the acid esters or the salts thereof of a polyadduct of 2 to 30 mol of ethylene oxide with 1 mol of a C₈-C₂₂fatty alcohol;
- the alkali metal salts, ammonium salts or amine salts of C₈-C₂₀fatty acids, which are termed soaps, typically coconut fatty acid;
- alkylamide sulfates;
- alkylamide ether sulfates;
- alkylaryl polyether sulfates;
- monoglyceride sulfates;

- 8 -

- alkane sulfonates, containing 8 to 20 carbon atoms in the alkyl chain, e.g. dodecyl sulfonate;
- alkylamide sulfonates;
- alkylaryl sulfonates;
- α -olefin sulfonates;
- sulfosuccinic acid derivatives, typically alkyl sulfosuccinates, alkyl ether sulfosuccinates or alkyl sulfosuccinamide derivatives;
- N-[alkylamidoalkyl]amino acids of formula



wherein

X is hydrogen, C_1 - C_4 alkyl or $-\text{COO}^-\text{M}^+$,

Y is hydrogen or C_1 - C_4 alkyl,

Z is $-(\text{CH}_2)_{m_1-1}$,

m_1 is 1 to 5,

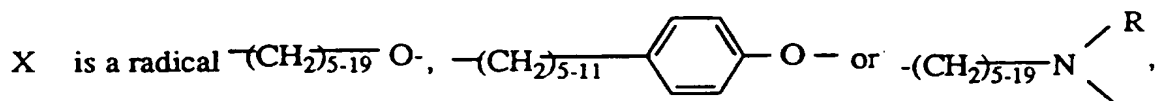
n is an integer from 6 to 18, and

M is an alkali metal ion or an amine ion;

- alkyl ether carboxylates and alkylaryl ether carboxylates of formula



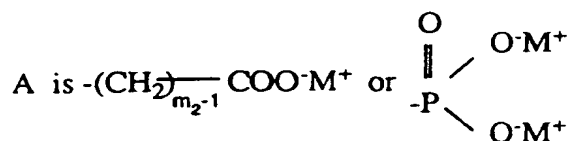
wherein



R is hydrogen or C_1 - C_4 alkyl,

Y is $-(\text{CHCHO})_{1-50}$,

- 9 -



m_2 is 1 to 6, and

M^+ is an alkali metal cation or amine cation.

The anionic surfactants used may furthermore be fatty acid methyl taurides, alkylisothionates, fatty acid polypeptide condensates and fatty alcohol phosphoric acid esters. The alkyl radicals in these compounds preferably contain 8 to 24 carbon atoms.

The fatty alcohols which may be present in the above-mentioned surfactants are those containing 8 to 22, preferably 8 to 18 carbon atoms, typically octyl, decyl, lauryl, tridecyl, miristyl, cetyl, stearyl, oleyl, arachidyl or behenyl alcohol.

The anionic surfactants are usually obtained in the form of their water-soluble salts, such as the alkali metal, ammonium or amine salts. Typical examples of such salts are lithium, sodium, potassium, ammonium, triethylamine, ethanolamine, diethanolamine or triethanolamine salts. It is preferred to use the sodium or potassium salts or the ammonium-($NR_1R_2R_3$) salts, wherein R_1 , R_2 and R_3 are each independently of one another hydrogen, C_1 - C_4 alkyl or C_1 - C_4 hydroxyalkyl.

The anionic surfactants preferably used in the formulation of this invention are C_8 - C_{22} fatty acid alcohol ether sulfates, more particularly the alkali metal salts of lauryl ether sulfate.

Very particularly preferred anionic surfactants in the novel formulation are monoethanolamine lauryl sulfate or the alkali metal salts of fatty alcohol sulfates, preferably the sodium lauryl sulfate and the reaction product of 2 to 4 mol of ethylene oxide and sodium lauryl ether sulfate.

Suitable zwitterionic and amphoteric surfactants are C_8 - C_{18} betaines, C_8 - C_{18} sulfobetaines, C_8 - C_{24} alkylamido- C_1 - C_4 alkylenebetaines, imidazoline carboxylates, alkylamphocarboxy carboxylic acids, alkylamphocarboxylic acids (e.g. lauroamphoglycinate) and N-alkyl- β -aminopropionates or N-alkyl- β -iminodipropionates. It is preferred to use the C_{10} - C_{20} alkylamido- C_1 - C_4 alkylenebetaines and, more particularly,

cocoamidopropylbetaine.

Nonionic surfactants are typically derivatives of the adducts of propylene oxide/ethylene oxide having a molecular weight of 1000 to 15000, fatty alcohol ethoxylates (1-50 EO), alkylphenol polyglycol ethers (1-50 EO), ethoxylated carbohydrates, fatty acid glycol partial esters, typically diethylene glycol monstearate, fatty acid alkanolamides and fatty acid dialkanolamides, fatty acid alkanolamide ethoxylates and fatty acid amine oxides. The fatty acid alkanolamides and fatty acid dialkanolamides and, preferably, cocodiethanolamide are to be particularly highlighted.

Suitable components (d) are the salts of saturated and unsaturated C₁₂-C₂₂ fatty acids, typically lauric, myristic, palmitic, stearic, arachic, behenic, dodecenoic, tetradecenoic, octadecenoic, oleic, eicosanic and erucic acid, as well as the technical mixtures of such acids, typically coconut fatty acid which is preferably used in the novel formulation. These acids may be obtained in the form of salts, suitable cations being alkali metal cations such as sodium and potassium cations, metal atoms such as zinc atoms and aluminium atoms or nitrogen-containing organic compounds of sufficient alkalinity, typically amines or ethoxylated amines. These salt can also be prepared in situ. Component (d) can also be a mixture of the indicated salts.

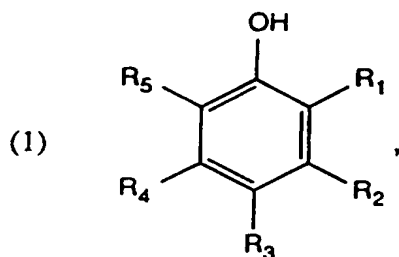
Suitable components (e) are dihydric alcohols, preferably those containing 2 to 6 carbon atoms in the alkylene radical, typically ethylene glycol, 1,2- or 1,3-propanediol, 1,3-, 1,4- or 2,3-butanediol, 1,5-pentanediol and 1,6-hexanediol. 1,2-propanediol (propylene glycol) is preferred.

Component (f) is preferably ethanol, n-propanol and isopropanol or a mixture of these alcohols.

Preferred novel formulations are those comprising

(a₁) a compound of formula

- 11 -



wherein

R₁ is hydrogen, hydroxy, C₁-C₄alkyl, chloro, nitro, phenyl or benzyl,

R₂ is hydrogen, hydroxy, C₁-C₆alkyl or chloro,

R₃ is hydrogen, C₁-C₆alkyl, hydroxy, chloro, nitro or a sulfo group in the form of the alkali metal salts or ammonium salts thereof,

R₄ is hydrogen or methyl, and

R₅ is hydrogen or nitro,

- (b) 0.1 to 25% by weight of a mixture of sodium cumene sulfonate and citric acid monohydrate,
- (c) 1 to 10% by weight of a C₈-C₂₂fatty acid alcohol ether sulfate,
- (e) 0 to 50% by weight of a dihydric alcohol;
- (f) 0 to 70% by weight of a monohydric alcohol or of a mixture of several monohydric alcohols; and
- (g) mains water or deionised water to make up 100%.

The pH of the novel formulation is 3 to 10, preferably 4.5 to 6.

The novel formulations obtained as soap or syndet solutions may additionally comprise customary additives, typically sequestrants, dyes, perfume oils, thickeners or solidifiers (consistency regulators), emollients, UV absorbers, skin-protection agents, antioxidants, additives which improve the mechanical properties, such as dicarboxylic acids and/or Al, Zn, Ca, Mg salts of C₁₄-C₂₂fatty acids and, if desired, preservatives.

The novel soap bars can be fabricated in per se known manner, typically by mixing the novel components (a) and (b) and, optionally, (c), (d), (e) and (f), as well as any additives in a jerk-mixer at 18-25°C. After the composition obtained has been processed, it is extruded at 40 to 60°, preferably from 45 to 50°C, and then cut and stamped in moulds.

Soap formulations of the invention can be prepared by mixing components (a) and (b) and, optionally, (c), (d), (e) and (f), in any order, with the requisite amount of water and stirring

- 12 -

the mixture to homogeneity. The mixture is bulked to 100% with additional water. This procedure is a purely physical procedure. Accordingly, there is no chemical reaction of the individual components.

For disinfection and cleansing of the human skin and hands and of hard objects, the novel soap formulations can be applied thereto in dilute or undilute form, suitably in an amount of at least 2 ml, preferably in the undilute form, for hand disinfection.

The invention is illustrated by the following Examples. Parts and percentages are by weight.

Example 1:

1.0 part	o-phenylphenol,
4.0 parts	sodium lauryl ether-2-sulfate,
8.0 parts	sodium cumene sulfonate powder,
8.0 parts	citric acid monohydrate,
10.0 parts	propylene glycol, and
water to make up 100 parts	

are stirred to homogeneity and about 90% of the requisite water is then added. The pH is adjusted to 5.5 with monoethanolamine. Deionised water is then added to the solution to make up a total of 100 parts. The pH is checked again and, if necessary, monoethanolamine is added to adjust the pH to 5.5.

Example 2:

1.0 part	o-phenylphenol,
4.0 parts	sodium lauryl ether-4-sulfate,
8.0 parts	sodium cumene sulfonate powder,
8.0 parts	citric acid monohydrate,
10.0 parts	propylene glycol, and
water to make up 100 parts	

is stirred to homogeneity and about 90% of the requisite water is then added. The pH is adjusted to 5.5 with monoethanolamine. Deionised water is then added to the solution to make up a total of 100 parts. The pH is checked again and, if necessary, monoethanolamine is added to adjust the pH to 5.5.

Example 3:

1.0 part p-chloro-m-xylene,
4.0 parts sodium lauryl ether-2-sulfate
8.0 parts sodium cumene sulfonate powder,
8.0 parts citric acid monohydrate,
10.0 parts propylene glycol, and
water to make up 100 parts

are mixed to homogeneity and about 90% of the requisite water is then added. The pH is adjusted to 5.5 with monoethanolamine. Deionised water is then added to the solution to make up a total of 100 parts. The pH is checked again and, if necessary, monoethanolamine is added to adjust the pH to 5.5.

Example 4:

1.0 part p-chloro-o-benzylphenol,
4.0 parts sodium lauryl ether-2-sulfate
8.0 parts sodium cumene sulfonate powder,
8.0 parts citric acid monohydrate,
10.0 parts propylene glycol, and
water to make up 100 parts

are stirred to homogeneity and about 90% of the requisite water is then added. The pH is adjusted to 5.5 with monoethanolamine. Deionised water is then added to the solution to make up a total of 100 parts. The pH is checked again and, if necessary, monoethanolamine is added to adjust the pH to 5.5.

Example 5:

2.0 parts benzyl alcohol,
4.0 parts sodium lauryl sulfate
5.0 parts sodium cumene sulfonate powder,
8.0 parts citric acid monohydrate,
10.0 parts propylene glycol, and
water to make up 100 parts

are stirred to homogeneity and about 90% of the requisite water is then added. The pH is adjusted to 5.5 with monoethanolamine. Deionised water is then added to the solution to make up a total of 100 parts. The pH is checked again and, if necessary, monoethanolamine is added to adjust the pH to 5.5.

Example 6:

4.0 parts cocamidopropylbetaine,
5.0 parts sodium cumene sulfonate,
10.0 parts propylene glycol,
8.0 parts citric acid monohydrate, and

water to make up 100 parts

are stirred to homogeneity and about 90% of the requisite water is then added. The pH is adjusted to 5.5 with monoethanolamine. Deionised water is then added to the solution to make up a total of 100 parts. The pH is checked again and, if necessary, monoethanolamine is added to adjust the pH to 4.0.

Example 7:

4.0 parts cocamidopropylbetaine,
12.0 parts ethanol,
8.0 parts citric acid monohydrate, and

water to make up 100 parts

are stirred to homogeneity and about 90% of the requisite water is then added. The pH is adjusted to 5.5 with monoethanolamine. Deionised water is then added to the solution to make up a total of 100 parts. The pH is checked again and, if necessary, monoethanolamine is added to adjust the pH to 4.0.

Example 8:

4.0 parts sodium lauraminopropionate,
5.0 parts sodium cumene sulfonate,
10.0 parts propylene glycol,
8.0 parts citric acid monohydrate, and

water to make up 100 parts

are stirred to homogeneity and about 90% of the requisite water is then added. The pH is adjusted to 5.5 with monoethanolamine. Deionised water is then added to the solution to make up a total of 100 parts. The pH is checked again and, if necessary, monoethanolamine is added to adjust the pH to 4.0.

Example 9:

4.0 parts sodium lauraminopropionate,
12.0 parts ethanol,
8.0 parts citric acid monohydrate, and

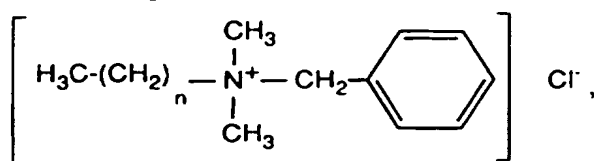
- 15 -

water to make up 100 parts

are stirred to homogeneity and about 90% of the requisite water is then added. The pH is adjusted to 5.5 with monoethanolamine. Deionised water is then added to the solution to make up a total of 100 parts. The pH is checked again and, if necessary, monoethanolamine is added to adjust the pH to 4.0.

Example 10:

1.0 part of the compound of formula



wherein n is an integer from 7 to 17,

4.0 parts cocamidopropylbetaine,

12.0 parts ethanol,

8.0 parts citric acid monohydrate, and

water to make up 100 parts

are stirred to homogeneity and about 90% of the requisite water is then added. The pH is adjusted to 5.5 with monoethanolamine. Deionised water is then added to the solution to make up a total of 100 parts. The pH is checked again and, if necessary, monoethanolamine is added to adjust the pH to 5.5.

Example 11:

1.0 part 2,4-dichlorobenzyl alcohol

4.0 parts sodium laurylsulfate,

5.0 parts sodium cumene sulfonate,

1.0 part propylene glycol,

8.0 parts citric acid monohydrate, and

water to make up 100 parts

are stirred to homogeneity and about 90% of the requisite water is then added. The pH is adjusted to 5.5 with monoethanolamine. Deionised water is then added to the solution to make up a total of 100 parts. The pH is checked again and, if necessary, monoethanolamine is added to adjust the pH to 5.5.

Example 12: Test of the microbicidal activity of the novel formulations

The microbicidal activity (in decimal logarithms) of the novel formulations according to Examples 1 to 11 is determined with a suspension test. This test is used to assess the bactericidal activity of water-soluble antiseptics, disinfectants and of liquid soaps. The test consists in seeding the test product in selected dilutions with the test bacillus. After a certain contact time, aliquots is taken and the number of surviving bacilli is determined. The difference between the number of the bacilli added and the number of the surviving bacilli is expressed as bacilli reduction in decimal logarithms. The concentration is 90%, the contact time is 30 seconds.

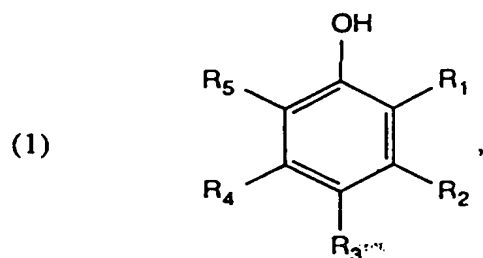
The following test bacilli are used:

<u>Example</u>	Staph. aureus ATCC 9144	Strept. faecalis ATCC 10,541	E. Coli ATCC 10,536	P.aeruginosa CIP A-22	Serratia mar- cescens ATCC 13,88
1	4.6	>5.1	>5.3	>5.3	>5.4
2	>5.5	>5.2	>5.1	>5.3	>5.5
3	>5.5	>5.2	>5.1	>5.3	>5.5
4	>5.5	>5.2	>5.1	>5.3	>5.5
5	>6	>6	>6	>6	>6
6	2.0	0.2	1.4	>6	2.7
7	0	0.5	2.6	>6	1.3
8	0.1	0.3	0.7	>6	2.5
9	3.5	>6	>6	>6	4.2
10	1.0	1.7	>6	>6	4.7
11	3.4	>6	>6	>6	>6

What is claimed is

1. A surface-active surfactant formulation, comprising

- (a) 0.01 to 5% by weight of a microbicidal active substance selected from the group consisting of
- (a₁) phenol derivatives,
 - (a₂) diphenyl compounds,
 - (a₃) benzyl alcohols,
 - (a₄) chlorohexidine,
 - (a₅) C₁₂-C₁₄alkylbetaines and C₈-C₁₈fatty acid amidoalkylbetaines,
 - (a₆) amphoteric surfactants,
 - (a₇) trihalocarbanilides, and
 - (a₈) quaternary ammonium salts;
- (b) 0.1 to 25% by weight of one or more than one hydrotropic agent;
- (c) 0 to 10% by weight of one or more than one synthetic surface-active substance or of a soap or of combinations of the cited substances;
- (d) 0 to 8% by weight of a salt of a saturated and/or unsaturated C₈-C₂₂fatty acid;
- (e) 0 to 50% by weight of a dihydric alcohol;
- (f) 0 to 70% by weight of a monohydric alcohol or of a mixture of several monohydric alcohols; and
- (g) mains water or deionised water to make up 100%,
- with the proviso that said formulations contain at least one of components (c) and (d).

2. A formulation according to claim 1, wherein the compounds used for component (a₁) are those of the general formula

wherein

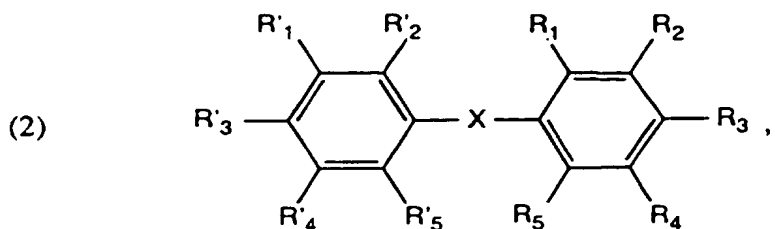
- R₁ is hydrogen, hydroxy, C₁-C₄alkyl, chloro, nitro, phenyl oder benzyl,
- R₂ is hydrogen, hydroxy, C₁-C₆alkyl or halogen,
- R₃ is hydrogen, C₁-C₆alkyl, hydroxy, chloro, nitro or a sulfo group in the form of the

alkali metal salts or ammonium salts thereof,

R_4 is hydrogen or methyl,

R_5 is hydrogen or nitro.

3. A formulation according to claim 1, wherein the compounds used for component (a_2) are those of formula



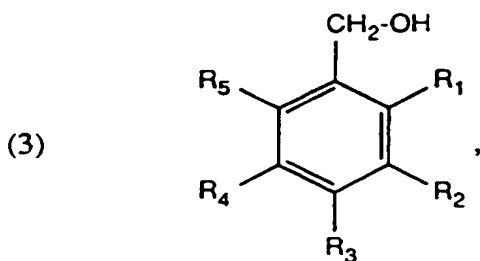
wherein

X is sulfur or the methylene group,

R_1 and R'_1 are hydroxy, and

R_2 , R'_2 , R_3 , R'_3 , R_4 , R'_4 , R_5 and R'_5 are each independently of one another hydrogen or halogen.

4. A formulation according to claim 1, wherein the compounds used for component (a_3) are those of formula



wherein

R_1 , R_2 , R_3 , R_4 and R_5 are each independently of one another hydrogen or chloro.

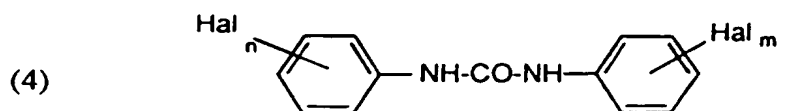
5. A formulation according to claim 1, wherein component (a_4) is chlorohexidine or a salt thereof with an organic or inorganic acid.

6. A formulation according to claim 1, wherein component (a_5) is cocamidopropylbetaine.

- 19 -

7. A formulation according to claim 1, wherein component (a₆) is a C₁₂alkylaminocarboxylic acid or a C₁-C₃alkanecarboxylic acid.

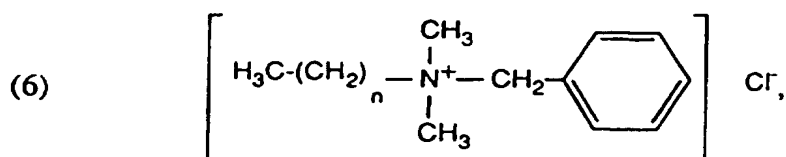
8. A formulation according to claim 1, wherein the compounds used for component (a₇) are those of the general formula



wherein

Hal is chloro or bromo,
n and m are 1 or 2, and
n + m are 3.

9. A formulation according to claim 1, wherein the compound used for component (a₈) is a compound of formula



wherein

n is an integer from 7 to 17.

10. A formulation according to any one of claims 1 to 9, wherein component (b₁) is a sulfonate, preferably a salt thereof of a terpenoid or of a mono- or binuclear aromatic compound.

11. A formulation according to claim 10, wherein the mono- or binuclear aromatic compounds are the sulfonates of camphor, toluene, xylene, cumene or naphthene.

12. A formulation according to any one of claims 1 to 11, wherein component (b) consists of only one compound of subclass (b₁) or also of a mixture of one or more than one compound of subclass (b₁) together with components of further subclasses.

- 20 -

13. A formulation according to any one of claims 1 to 11, wherein component (b) is a combination of one or more than one compound of subclass (b₁) and one or more than one compound of subclass (b₂).

14. A formulation according to claim 13, wherein a combination of cumene sulfonate and citric acid monohydrate is used.

15. A formulation according to any one of claims 1 to 14, wherein component (c) is an anionic surfactant in the form of the water-soluble salt thereof.

16. A formulation according to claim 15, wherein component (c) is C₈-C₂₂fatty alcohol ether sulfate.

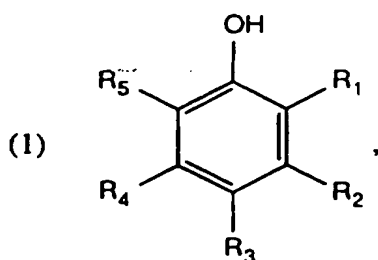
17. A formulation according to claim 16, wherein component (c) is an alkali metal salt of lauryl ether sulfate.

18. A formulation according to any one of claims 1 to 17, wherein component (d) is selected from the group consisting of lauric, myristic, palmitic, stearic, arachic, behenic, dodecenic, tetradecenic, octadecenic, oleic, eicosenic and erucic acid.

19. A formulation according to any one of claims 1 to 18, wherein component (e) is propylene glycol.

20. A formulation according to any one of claims 1 to 19, wherein component (f) is selected from the group consisting of ethanol, propanol, isopropanol, and mixtures of these alcohols.

21. A surface-active formulation comprising
(a₁) a compound of formula



- 21 -

wherein

- R_1 is hydrogen, hydroxy, C_1 - C_4 alkyl, chloro, nitro, phenyl oder benzyl,
 R_2 is hydrogen, hydroxy, C_1 - C_6 alkyl or halogen,
 R_3 is hydrogen, C_1 - C_6 alkyl, hydroxy, chloro, nitro or a sulfo group in the form of the alkali metal salts or ammonium salts thereof,
 R_4 is hydrogen or methyl,
 R_5 is hydrogen or nitro,
(b) 0.1 to 25% by weight of a mixture of sodium cumene sulfonate and citric acid monohydrate,
(c) 0 to 10% by weight of a C_8 - C_{22} fatty alcohol ether sulfate,
(d) 0 to 50% by weight of a dihydric alcohol,
(e) 0 to 70% by weight of a monohydric alcohol or of a mixture of several monohydric alcohols, and
(f) mains water or deionised water to make up 100%.

22. Use of an antimicrobial soap formulation as claimed in any one of claims 1 to 21 for the disinfection and cleansing of the human skin and hands and of hard objects.

THIS PAGE BLANK (USPTO)

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification: C11D 3/00, A61K 7/48, 7/50	A3	(11) International Publication Number: WO 96/06153 (43) International Publication Date: 29 February 1996 (29.02.96)
(21) International Application Number: PCT/EP95/03211 (22) International Filing Date: 14 August 1995 (14.08.95) (30) Priority Data: 2611/94-8 25 August 1994 (25.08.94) CH (71) Applicant (for all designated States except US): CIBA-GEIGY AG [CH/CH]; Klybeckstrasse 141, CH-4002 Basle (CH). (72) Inventor; and (75) Inventor/Applicant (for US only): MOLDOVANYI, Laszlo [CH/CH]; Oberer Batterieweg 15, CH-4059 Basle (CH). (74) Common Representative: CIBA-GEIGY AG; Patentabteilung, Klybeckstrasse 141, CH-4002 Basle (CH).		(81) Designated States: AM, AU, BB, BG, BR, BY, CA, CN, CZ, EE, FI, GE, HU, IS, JP, KG, KP, KR, KZ, LK, LR, LT, LV, MD, MG, MK, MN, MX, NO, NZ, PL, RO, RU, SG, SI, SK, TJ, TM, TT, UA, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, MW, SD, SZ, UG). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i> (88) Date of publication of the international search report: 2 May 1996 (02.05.96)
(54) Title: SURFACE-ACTIVE FORMULATIONS (57) Abstract The invention relates to surface-active soap formulations, comprising: (a) 0.01 to 5 % by weight of a microbicidal active substance selected from the group consisting of (a ₁) phenol derivatives (a ₂) diphenyl compounds (a ₃) benzyl alcohols (a ₄) chlorohexidine (a ₅) C ₁₂ -C ₁₄ alkylbetaines and C ₈ -C ₁₈ fatty acid amidoalkylbetaines (a ₆) amphoteric surfactants and (a ₇) trihalocarbanilides; (b) 0.1 to 25 % by weight of one or more than one hydrotropic agent; (c) 0 to 10 % by weight of one or more than one synthetic surface-active substance or of a soap or of combinations of the cited substances; (d) 0 to 8 % by weight of a salt of a saturated and/or unsaturated C ₈ -C ₂₂ fatty acid; (e) 0 to 50 % by weight of a dihydric alcohol; (f) 0 to 70 % by weight of a monohydric alcohol or of a mixture of several monohydric alcohols; and (g) mains water or deionised water to make up 100 %, with the proviso that the formulations contain at least one of components (c) and (d). The formulations are used for the disinfection and cleansing of the human skin and hands and of hard objects.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LJ	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Larvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 95/03211

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C11D3/00 A61K7/48 A61K7/50

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C11D A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE,A,37 23 990 (CIBA-GEIGY AG.) 4 February 1988 see the whole document ---	1,3,6, 15-17, 19,20,22
X	CH,A,552 670 (UNILEVER PLC) 15 August 1974 see the whole document ---	1,3,8,22
X	GB,A,1 408 885 (CIBA-GEIGY AG.) 8 October 1975 see the whole document ---	1,3,10, 11,15, 16,20,22
X	FR,A,1 501 612 (HENKEL KOMMANDIT GESELLSCHAFT AUF AKTIEN) 31 January 1968 see the whole document ---	1-3,8, 10,11, 15,16, 20,22
-/-		

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *&* document member of the same patent family

Date of the actual completion of the international search

22 February 1996

Date of mailing of the international search report

07.03.96

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,
Fax (+ 31-70) 340-3016

Authorized officer

Couckuyt, P

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>DATABASE WPI Week 8941 Derwent Publications Ltd., London, GB; AN 89-292819 & AU,A,3 001 889 (CIBA-GEIGY AG.) , 17 August 1989 see abstract</p>	1,3,22
X	<p>DE,A,31 17 792 (SCHÜLKE & MAYR GMBH) 18 November 1982 see the whole document</p>	1-3,9, 20-22
X	<p>FR,A,2 301 233 (BEECHAM GROUP LIMITED) 17 September 1976 see the whole document</p>	1-3,9, 20-22
X	<p>EP,A,0 433 911 (KAO CORPORATION) 26 June 1991 see the whole document</p>	1-3,8,9, 19-22
X	<p>DE,A,37 23 994 (CIBA-GEIGY AG.) 4 February 1988 see the whole document</p>	1,3,15, 16,20,22
X	<p>DATABASE WPI Week 9347 Derwent Publications Ltd., London, GB; AN 93-374809 & JP,A,05 279 693 (SHINETSU CHEM IND CO LTD) , 26 October 1992 see abstract</p>	1,3,22
X	<p>EP,A,0 047 033 (THE PROCTER & GAMBLE COMPANY) 10 March 1982 see the whole document</p>	1,8,22
A	<p>US,A,4 832 861 (RESCH) 23 May 1989 see the whole document</p>	1-6,15, 19,20
A	<p>DE,A,22 61 030 (BASF WYANDOTTE CORP.) 20 December 1972 see the whole document</p>	1,22
A	<p>DATABASE WPI Week 8829 Derwent Publications Ltd., London, GB; AN 88-202120 & JP,A,63 139 998 (LION CORP.) , 11 June 1988 see abstract</p>	1,3,8,22
A	<p>WO,A,94 10837 (WEST AGRO INC.) 26 May 1994 see the whole document</p>	1,22

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 95/03211

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE-A-3723990	04-02-88	NONE	
CH-A-552670	15-08-74	DE-A- 2044309 FR-A- 2064811 GB-A- 1266060 NL-A- 7013370 SE-A,C 386202	22-04-71 23-07-71 08-03-72 16-03-71
GB-A-1408885	08-10-75	NONE	
FR-A-1501612	31-01-68	BE-A- 690213 CH-A- 484268 DE-A- 1467619 NL-A- 6615294 US-A- 3503885	25-05-67 15-01-70 13-02-69 29-05-67 31-03-70
DE-A-3117792	18-11-82	NONE	
FR-A-2301233	17-09-76	GB-A- 1539031 AU-B- 500125 AU-B- 1134076 DE-A- 2606462	24-01-79 10-05-79 01-09-77 02-09-76
EP-A-433911	26-06-91	JP-A- 3193727	23-08-91
DE-A-3723994	04-02-88	NONE	
EP-A-47033	10-03-82	US-A- 4310433 AU-B- 543478 AU-B- 7481681 CA-A- 1151495 DE-A- 3176819 JP-A- 57115500	12-01-82 18-04-85 11-03-82 09-08-83 01-09-88 17-07-82
US-A-4832861	23-05-89	CA-A- 1332555 US-A- 4954281 US-A- 5006529	18-10-94 04-09-90 09-04-91
DE-A-2261030	20-06-73	DE-A- 2260971 FR-A,B 2163577	28-06-73 27-07-73

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 95/03211

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE-A-2261030		GB-A- 1403919	28-08-75
		GB-A- 1404860	03-09-75
		SE-A,B,C 376928	
		SE-A,B,C 376929	

WO-A-9410837	26-05-94	AU-B- 5129793	08-06-94
		CA-A- 2148921	26-05-94
		US-A- 5330769	19-07-94
		US-A- 5391379	21-02-95
